

## PATENT ABSTRACTS OF JAPAN

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(71)Applicant : MITSUBISHI HEAVY IND LTD

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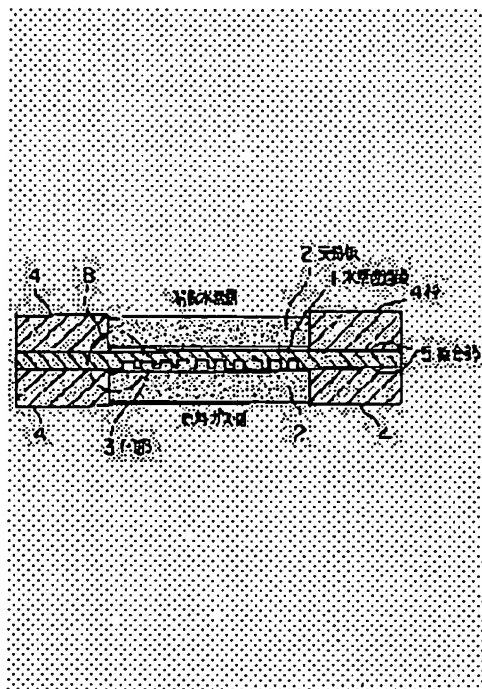
(72)Inventor : KOBAYASHI TOSHIRO  
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### (54) HYDROGEN SEPARATING MEMBRANE UNIT

#### (57)Abstract:

PURPOSE: To improve strength, durability to repetitive use and hydrogen permeation performance by using metallic or alloy foil provided with many recessed parts in hydrogen permeating parts of a hydrogen permeable membrane.

CONSTITUTION: The hydrogen permeable membrane 1 formed with the recessed parts 3 in a square-meshed form is sandwiched by metallic frames 4 joined with supporting plates 2 consisting of perforated metallic plates and are joined by joining parts 5. The hydrogen permeable membrane 1 consists of Pd and alloys, such as Pd-Ag, Pd-Y, Pd-Ni and Pd-Cu and is so formed as to attain  $t_0 > t_2 = t_3$  when the film thickness is defined as  $30$  to  $50\mu\text{m}$  ( $t_3$ ) de, the depth of the recessed parts as  $t_1$ , the film thickness of the recessed parts as  $t_2$  and the film thickness by the conventional method as  $t_0$ . The pitch of the recessed parts 3 is determined by taking the ratio (30 to 90%) of the area of the recessed parts 3 to the area over the entire part of the hydrogen permeable membrane and the strength, etc., over the entire part of the membrane into consideration. The recessed parts 3 described above may be formed on any of the gaseous raw material side, refined hydrogen side and both sides of the hydrogen permeable membrane 1.



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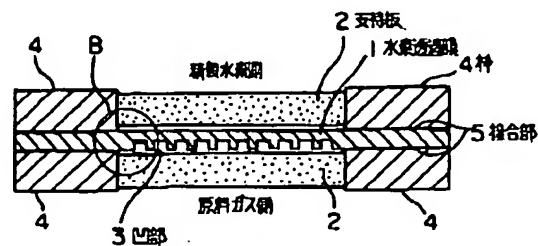
(54) 【発明の名称】 水素分離膜ユニット

(57) 【要約】

【目的】 水素精製装置や水素製造装置に適用される水素分離膜ユニットに関する。

【構成】 金属又は合金箔製の水素透過膜の周囲を両面から金属製の枠ではさんで固定し、前記水素透過膜の少くとも精製水素側の面を周囲が前記金属製の枠に接合された金属多孔質材からなる支持板で支持した水素分離膜ユニットにおいて、前記水素透過膜として水素の透過部分に多数の凹部を設けた金属又は合金箔製の水素透過膜を使用したことを特徴とする水素分離膜ユニット。

【効果】 従来の水素分離膜ユニットに比較し水素透過性能は同等以上であり、強度が著しく改善され、長時間の繰返し使用に対する耐性が格段に優れている。



## 【特許請求の範囲】

【請求項1】 金属又は合金箔製の水素透過膜の周囲を両面から金属製の枠ではさんで固定し、前記水素透過膜の少くとも精製水素側の面を周囲が前記金属製の枠に接合された金属多孔質材からなる支持板で支持した水素分離膜ユニットにおいて、前記水素透過膜として水素の透過部分に多数の凹部を設けた金属又は合金箔製の水素透過膜を使用したことを特徴とする水素分離膜ユニット。

【請求項2】 水素透過膜に設けた凹部がディンプル状又は升目状に形成されていることを特徴とする請求項1に記載の水素分離膜ユニット。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】 本発明は水素精製装置や水素製造装置に適用される水素分離膜ユニットに関する。

## 【0002】

【従来の技術】 図8に従来の水素分離膜ユニットの断面図の1例を示す。図8の水素分離膜ユニットでは枠4に溶接部5'で溶接され補強された金属多孔質材（金網を含む）からなる支持板2の間に水素（H<sub>2</sub>）のみを透過する性質を有するPd又はPd合金箔からなる水素透過膜1をはさみ、接合部5でろう付、拡散接合、溶接等により接合されている。稼動時には高温下で原料ガス側に水素を含む原料ガスを流すことにより、水素のみが選択的に水素透過膜を通過して原料ガス側から精製水素側へ拡散、移動し、精製水素側で高純度の水素が得られる。このときの水素の透過速度は水素透過膜の厚さtに反比例し、膜の厚さtが薄ければ薄いほど高い水素分離性能が得られる。また、原料ガス側の圧力P<sub>1</sub>と精製水素側の圧力P<sub>2</sub>との差圧 $\Delta P = P_1 - P_2$ が大きい方が水素透過速度が大きくなり、高性能となる。

## 【0003】

【発明が解決しようとする課題】 図8に示すような水素分離膜ユニットにおいては、支持板2は枠4に溶接により接合されている。このような接合の場合、通常図8のA部の使用時の状態を示す拡大図である図7に示すように枠4の水素透過膜1に接する面と支持板2の水素透過膜1に平行な面との間に段差aが生じる。また、金網を含む金属多孔板で形成される支持板2の表面には多数の凹凸がある。このような水素分離膜ユニットにおいて、水素分離性能を向上させるため $\Delta P$ を大きくし、tを小さくしようとすると次のような問題がある。

(1) 段差a部で水素透過膜1に局部的な歪6が加わり破断する恐れがある。

(2) 水素透過膜1が支持板2に押しつけられ、支持板表面の凹部にくい込み、大きな歪を受けて破断する恐れがある。

【0004】 本発明は前記技術水準に鑑み、従来技術における水素透過膜の破断を防止することができる水素分離膜ユニットを提供しようとするものである。

## 【0005】

【課題を解決するための手段】 本発明は(1) 金属又は合金箔製の水素透過膜の周囲を両面から金属製の枠ではさんで固定し、前記水素透過膜の少くとも精製水素側の面を周囲が前記金属製の枠に接合された金属多孔質材からなる支持板で支持した水素分離膜ユニットにおいて、前記水素透過膜として水素の透過部分に多数の凹部を設けた金属又は合金箔製の水素透過膜を使用したことを特徴とする水素分離膜ユニット及び(2) 水素透過膜に設けた凹部がディンプル状又は升目状に形成されていることを特徴とする前記(1)の水素分離膜ユニットである。

【0006】 本発明の水素分離膜ユニットにおいては、従来この種の水素分離膜ユニットに使用されている厚さ約20 $\mu$ mの水素透過膜に代えて厚さ30～50 $\mu$ mの水素透過膜を使用する。これによって水素透過膜の強度が増加するので、枠と支持板との接合部の段差による局部的な歪による破断を防ぐことができ、また支持板表面の凹部へのくい込みを少なくすることができる。厚みが30 $\mu$ m未満では強度向上の効果がなく、50 $\mu$ mを超えると凹部を薄く加工することが困難である。

【0007】 このように水素透過膜の厚みを厚くすると水素透過性が悪くなるので水素透過部分の表面に多数の凹部、すなわち膜厚の薄い部分を設け水素の透過性を確保する。凹部の深さt<sub>1</sub>は、凹部のない部分の膜厚をt<sub>0</sub>、凹部における膜厚をt<sub>1</sub>、従来方法における膜厚をt<sub>0</sub>とした場合にt<sub>0</sub>>t<sub>1</sub>=t<sub>0</sub>-t<sub>1</sub>となるようにするのが望ましい。凹部の形状としては特に制限はなく、図4に示す升目状、図5に示すディンプル状など膜の材質、形状等に応じて適当な形状とすればよい。水素透過膜の凹部のピッチ(l<sub>1</sub>)は凹部の面積の水素透過面全体の面積に対する割合と膜全体の強度等を考慮して適宜定めればよい。なお、支持板として使用する金属支持板の表面にも凹凸がある。通常、金属多孔板の凹部のピッチは明確ではないが、大まかな傾向としてそのピッチを(l<sub>2</sub>)とした場合l<sub>2</sub><l<sub>1</sub>となると水素透過膜が破損しやすくなる恐れがあるので、(l<sub>1</sub>)は支持板表面の凹部のピッチ(l<sub>2</sub>)より小さくなるようにするのが望ましい。また、凹部の面積は水素透過面全体の面積の30～90%程度とする。30%未満では水素透過性が悪く、90%を超えると強度が低下するので好ましくない。

【0008】 本発明の水素分離膜ユニットにおける水素透過膜の材質としてはPdのほかPd-Ag、Pd-Y、Pd-Ni、Pd-CuなどのPd合金あるいはPdに前記のAgなどの添加金属を複合して加えた三元合金なども使用することができる。

【0009】 前記の凹部は水素透過膜の原料ガス側、精製水素側のどちらに設けてもよく、両面に設けてもよい。このような凹部はパターンニング後エッチングするな

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どの方法により形成させることができる。

【0010】本発明の水素分離膜ユニットは前記の凹部を設けた水素透過膜の周囲の凹部が形成されていない部分を、両面から金属多孔質材からなる支持板が接合された金属製の枠ではさみ、ろう付け、拡散接合あるいは溶接により固定した構成となっている。なお、使用条件等により原料ガス側の支持板は省略してもよい。また、ここでいう金属多孔質材とは金網状あるいは不織布の形状を含むものである。

【0011】本発明の水素分離膜ユニットの1例について、その断面図を図1に示す。図1において升目状の凹部3が形成された水素透過膜1が、金属多孔材からなる支持板2が接合された金属製の枠4により凹部が形成されていない部分ではさまれ、接合部5で接合されている。この例では凹部は原料ガス側に形成されている。

【0012】図2及び図3にそれぞれ本発明の水素分離膜ユニットの他の例を示す。図2は水素透過膜1の升目状の凹部3が精製水素側に形成された例である。水素透過膜1の保持形態としては図1のように原料ガス側に凹部3を設け、精製水素側を平坦にし、その面を支持板2に接触させて保持するのが望ましいが、水素の透過性能には差はない。図3は図1の構造の原料ガス側の支持板2が省略された例であるが、水素の透過性能、膜の保持効果は変わらない。

【0013】

【作用】水素透過膜として従来使用されているものより厚いものを用いるようにしたことにより、図1のB部の使用時の拡大図である図6に示すように、図7に見られる局所的な歪6の発現が抑制され、 $\Delta P$ をより大きくしても破断し難くなる。また、水素透過部分に凹部を設けることにより、凸部の厚さ $t_1$ に相当する厚みを有する水素透過膜に近い剛性が得られ、かつ、凹部の厚さ $t_2$ に相当する厚さの水素透過膜に近い優れた水素透過性能が得られる。

【0014】

【実施例】以下実施例により本発明をさらに具体的に説明する。図1の形状の水素分離膜ユニットを作製し性能評価試験を行った。まずSUS316製の枠4とSUS316製で厚さ0.8mmで平均孔径(凹部のピッチ)1、が約30 $\mu$ mの金属多孔体(平均繊維径1.5 $\mu$ m、平均孔径30 $\mu$ mの不織布)からなる支持板2を溶接により接合した。この支持板2を接合した枠4の間に、図4に示すように一辺15 $\mu$ mの正方形で深さ25

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$\mu$ mの升目状の凹部を25 $\mu$ mのピッチで形成させた厚さ40 $\mu$ mのPd-20wt%Ag合金圧延箔からなる水素透過膜1をはさんで接合し、約120mm $\times$ 70mmの大きさの水素分離膜ユニットを作製した。この例では図6のaに相当する段差は20 $\mu$ mであった。

【0015】凹部を形成させた水素透過膜は次のようにして作製した。すなわち、厚さ40 $\mu$ mのPd-20wt%Ag合金圧延箔をアルカリ洗浄液中で超音波洗浄し、真空中で乾燥後、ポジタイプのレジスト材(東京応化製TSMR8800)を両面にコーターで塗付し、90℃で30分間加熱乾燥後、ピッチ25 $\mu$ m、一辺15 $\mu$ mの正方形のマスクを用い、片面に紫外線を露光した後、レジスト剥離液(東京応化製NMD-W)中で一辺15 $\mu$ mの正方形部のレジスト材を除去した。その後、120℃のフッ酸中で30分間保持し、一辺15 $\mu$ mの正方形部をエッチング除去した。その結果、正方形凹部の深さは約25 $\mu$ mであった。

【0016】比較試料として水素透過膜1を厚さ20 $\mu$ mのPd-20wt%Ag合金圧延箔としたほかは前記と同様にして図8の構造の水素分離膜ユニットを作製した。

【0017】このようにして作製した試料について箔の破断試験及び水素透過性能により性能評価を行った。まず箔の破断については、Ar中で原料側( $P_1$ )と精製水素側( $P_2$ )の差圧 $\Delta P = P_1 - P_2 = 9 \text{ kgf/cm}^2$ として( $P_2$ は真空)昇温速度300℃/Hrで600℃に加熱し、30分間保持後、冷却速度300℃/Hrで室温まで下げる履歴を繰返した。また、水素透過性能は差圧を9 $\text{kgf/cm}^2$ とし、原料ガス側を99%以上の水素を含む標準水素ガスとし、550℃で精製水素側に透過してくる水素の量から水素透過速度を測定した。

【0018】試験に用いた試料の形状及び性能評価試験結果を表1に示す。表1からわかるように破断試験においては従来方法による比較例の試料では、9回目に箔が破断し $P_2$ の圧力が上昇した。これに対し本発明による実施例の試料では、50回の繰返しによっても破断しなかった。また、水素透過速度は比較例では180 $\text{cm}^3 / (\text{cm}^2 \cdot \text{min} \cdot \text{atm}^{0.5})$ であるのに対し、本発明の実施例では230 $\text{cm}^3 / (\text{cm}^2 \cdot \text{min} \cdot \text{atm}^{0.5})$ と高い値が得られた。

【0019】

【表1】

5		6							
支持板 (金属多孔体)			水素透過膜 (Pd-Ag膜)				試 験 結 果		
厚さ ( $\mu\text{m}$ )	枠との 段差 ( $\mu\text{m}$ )	厚さ ( $\mu\text{m}$ ) $t_3$	升目状凹部 ( $\mu\text{m}$ )				温度昇降繰返し 箱の破断までの 回数	水素透過性能 $\text{cm}^3/(\text{cm}^2 \cdot \text{min} \cdot \text{atm}^{0.5})$	
			凹部 深さ $t_1$	凹部 厚さ $t_2$	凹凸の ピッチ $l_1$	凹部の 一辺			
比較例	800	20	20	-	-	-	-	7	180
実施例			40	25	15	25	15	50回でも 破断せず	230

## 【0020】

【発明の効果】本発明の水素分離膜ユニットは、従来の水素分離膜ユニットに比較すると、強度が著しく改善され、長時間の繰返し使用に対する耐性が格段に優れており、しかも水素透過性能は同等以上である。

## 【図面の簡単な説明】

【図1】本発明の水素分離膜ユニットの1例を示す断面図。

【図2】本発明の水素分離膜ユニットの他の1例を示す断面図。

【図3】本発明の水素分離膜ユニットの他の1例を示す断面図。

【図4】本発明に係る水素透過膜の升目状凹部の1例を示す拡大図。

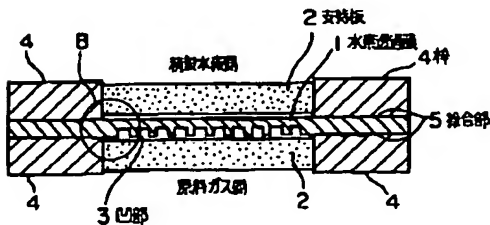
20 【図5】本発明に係る水素透過膜のディンプル状凹部の1例を示す拡大図。

【図6】図1のB部の使用時の状態を示す拡大図。

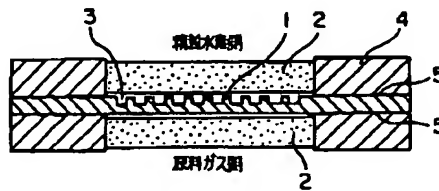
【図7】図8のA部の使用時の状態を示す拡大図。

【図8】従来の水素分離膜ユニットの1例を示す断面図。

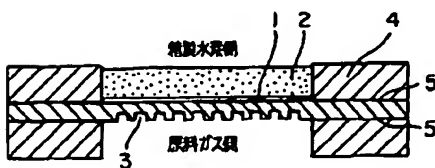
【図1】



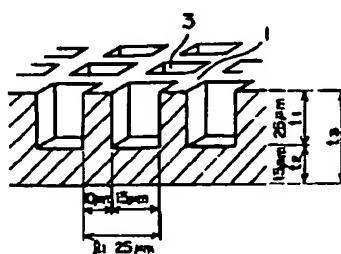
【図2】



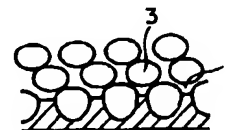
【図3】



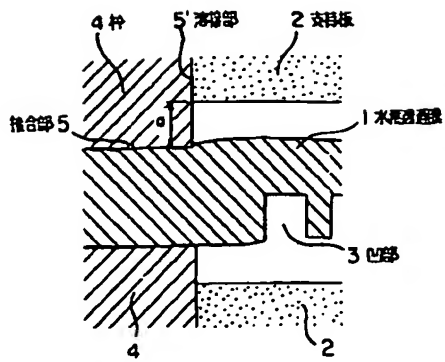
【図4】



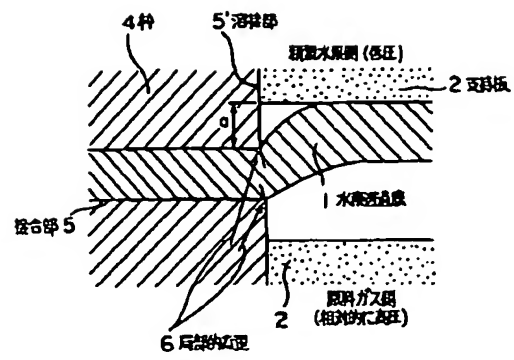
【図5】



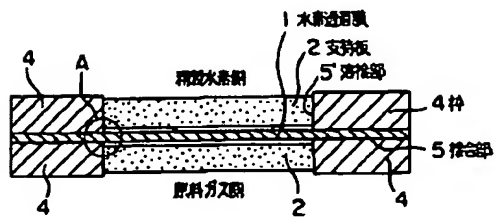
【図6】



【図7】



【図8】



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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the hydrogen demarcation membrane unit applied to a hydrogen refiner or a hydrogen manufacturing installation.

[0002]

[Description of the Prior Art] One example of the sectional view of the conventional hydrogen demarcation membrane unit is shown in drawing 8. In the hydrogen demarcation membrane unit of drawing 8, the hydrogen permeable film 1 which consists of Pd which has the property which penetrates only hydrogen (H<sub>2</sub>), or a Pd alloy foil is inserted between the support plates 2 which consist of metal porosity material (a wire gauze is included) which was welded and was reinforced with weld zone 5', and it is joined to the frame 4 by brazing, diffused junction, welding, etc. by the joint 5. By passing the material gas which contains hydrogen in a material gas side under an elevated temperature at the time of operation, only hydrogen passes a hydrogen permeable film selectively, and spreads and moves to a purification hydrogen side from a material gas side, and the hydrogen of a high grade is obtained by the purification hydrogen side. The hydrogen separation engine performance higher as membranous thickness  $t$  of the transmission rate of the hydrogen at this time is thin in inverse proportion to thickness  $t$  of a hydrogen permeable film is obtained. Moreover, pressure  $P_1$  by the side of material gas Pressure  $P_2$  by the side of purification hydrogen Differential pressure  $\Delta P = P_1 - P_2$  A hydrogen permeation rate becomes large and the larger one serves as high performance.

[0003]

[Problem(s) to be Solved by the Invention] In the hydrogen demarcation membrane unit as shown in drawing 8, the support plate 2 is joined to the frame 4 by welding. In such junction, a level difference arises between the field which touches the hydrogen permeable film 1 of a frame 4 as shown in drawing 7 which is the enlarged drawing usually showing the condition at the time of the activity of the A section of drawing 8, and a field parallel to the hydrogen permeable film 1 of a support plate 2. Moreover, much irregularity is shown in the front face of the support plate 2 formed with the metal perforated plate containing a wire gauze. In such a hydrogen demarcation membrane unit, in order to raise the hydrogen separation engine performance, when  $\Delta P$  tends to be enlarged and it is going to make  $t$  small, there are the following problems.

(1) There is a possibility that the local distortion may add and fracture to a hydrogen permeable film 1 in the level difference a section.

(2) A hydrogen permeable film 1 is pushed against a support plate 2, and there is a possibility of fracturing in response to a pile lump and a big distortion to the crevice on the front face of a support plate.

[0004] This invention tends to offer the hydrogen demarcation membrane unit which can prevent fracture of the hydrogen permeable film in the conventional technique in view of said technical level.

[0005]

[Means for Solving the Problem] This invention is fixed across the perimeter of the hydrogen permeable film made from (1) metal or an alloy foil by the metal frame from both sides. In the hydrogen demarcation membrane unit supported at least with the support plate which consists of metal porosity material of said hydrogen permeable film by which the perimeter was joined to said metal frame in the field by the side of purification hydrogen As said hydrogen permeable film hydrogen -- transparency -- a part -- a large number -- a crevice -- having prepared -- a metal -- or -- an alloy -- a foil -- make -- a hydrogen permeable film -- having used it -- things -- the description -- \*\* -- carrying out --

hydrogen -- a demarcation membrane -- a unit -- and -- (two --) -- a hydrogen permeable film -- having prepared -- a crevice -- a dimple -- \*\* -- or -- a grid -- \*\* -- forming -- having -- \*\*\*\* -- things -- the description -- \*\* -- carrying out -- the above -- (one --) -- hydrogen -- a demarcation membrane -- a unit -- it is .

[0006] In the hydrogen demarcation membrane unit of this invention, it replaces with a hydrogen permeable film with a thickness of about 20 micrometers currently conventionally used for this kind of hydrogen demarcation membrane unit, and a hydrogen permeable film with a thickness of 30-50 micrometers is used. Since the reinforcement of a hydrogen permeable film increases by this, the that it is lump which can prevent the local fracture by the level difference of the joint of a frame and a support plate depended distorted, and goes away to the crevice on the front face of a support plate can be lessened. If there is no effectiveness of the improvement in on the strength of thickness in less than 30 micrometers and it exceeds 50 micrometers, it is difficult to process a crevice thinly.

[0007] Thus, since hydrogen permeability will worsen if thickness of a hydrogen permeable film is thickened, many crevices, i.e., the thin part of thickness, are established in the front face of a hydrogen permeation part, and the permeability of hydrogen is secured. the depth  $t_1$  of a crevice thickness [ in / for thickness / in / for the thickness of a part without a crevice /  $t_3$  and a crevice /  $t_2$  and the conventional approach ] --  $t_0$  \*\* -- the case where it carries out --  $t_0 > t_2 = t_3 - t_1$  It is desirable to make it become. What is necessary is for there to be especially no limit and just to make it into a suitable configuration according to membranous construction material, configurations, etc., such as the shape of a grid shown in drawing 4 , and the shape of a dimple which are shown in drawing 5 , as a configuration of a crevice. What is necessary is just to determine suitably the pitch ( $l_1$ ) of the crevice of a hydrogen permeable film as the rate to the area of the whole hydrogen permeation side of the area of a crevice in consideration of the reinforcement of the whole film etc. In addition, irregularity is shown also in the front face of the metal support plate used as a support plate. Usually, the pitch of the crevice of a metal perforated plate is  $l_2 < l_1$  when the pitch is set to ( $l_2$ ) as a rough inclination, although it was not clear. Since there is a possibility of becoming easy to damage a hydrogen permeable film when it becomes, as for ( $l_1$ ), it is more desirable than the pitch ( $l_2$ ) of the crevice on the front face of a support plate to make it become small. Moreover, area of a crevice is made into about 30 - 90% of the area of the whole hydrogen permeation side. At less than 30%, since reinforcement will fall if hydrogen permeability is bad and exceeds 90%, it is not desirable.

[0008] The ternary alloy which compounded and added addition metals, such as aforementioned Ag, to Pd alloy or Pd, such as Pd-Ag, Pd-Y, Pd-nickel, and Pd-Cu, besides Pd as construction material of the hydrogen permeable film in the hydrogen demarcation membrane unit of this invention can be used.

[0009] The aforementioned crevice may be established in whichever by the side of the material gas of a hydrogen permeable film, and purification hydrogen, and may be established in both sides. Such a crevice can be made to form by the approach of etching after patterning.

[0010] The part of the hydrogen demarcation membrane unit of this invention in which the crevice around [ in which the aforementioned crevice was established ] a hydrogen permeable film is not formed is pinched by the metal frame to which the support plate which consists of metal porosity material was joined from both sides, and it has composition fixed by soldering, diffused junction, or welding. In addition, the support plate by the side of material gas may be omitted according to a service condition etc. Moreover, metal porosity material here includes the shape of a wire gauze, and the configuration of a nonwoven fabric.

[0011] About one example of the hydrogen demarcation membrane unit of this invention, the sectional view is shown in drawing 1 . It is inserted in the part in which the crevice is not formed with the metal frame 4 to which the support plate 2 with which the hydrogen permeable film 1 with which the grid crevice 3 was formed in drawing 1 consists of metal porosity material was joined, and is joined by the joint 5. The crevice is formed in the material gas side in this example.

[0012] Other examples of the hydrogen demarcation membrane unit of this invention are shown in drawing 2 and drawing 3 , respectively. Drawing 2 is the example by which the grid crevice 3 of a hydrogen permeable film 1 was formed in the purification hydrogen side. A crevice 3 is established in a material gas side like drawing 1 as retention form of a hydrogen permeable film 1, a purification hydrogen side is made flat, and although it is desirable to contact the field to a support plate 2, and to hold it, there is no difference in the penetrable ability of hydrogen. Although drawing 3 is the example to which the support plate 2 by the side of the material gas of the structure of drawing 1 was abbreviated, the penetrable ability of hydrogen and the membranous maintenance effectiveness do not change.

[0013]

[Function] As shown in drawing 6 which is an enlarged drawing at the time of the activity of the B section of drawing 1, even if the manifestation of the local distortion 6 looked at by drawing 7 is controlled and it enlarges  $P$  more, it is hard coming to fracture by having used the thing thicker than what is conventionally used as a hydrogen permeable film. Moreover, it is the thickness  $t_3$  of heights by establishing a crevice in a hydrogen permeation part. The rigidity near the hydrogen permeable film which has corresponding thickness is acquired, and it is the thickness  $t_1$  of a crevice. The outstanding hydrogen permeability ability near the hydrogen permeable film of corresponding thickness is obtained.

[0014]

[Example] An example explains this invention still more concretely below. The hydrogen demarcation membrane unit of the configuration of drawing 1 was produced, and the performance evaluation test was performed. It is the average aperture (pitch of a crevice)  $l_2$  in 0.8mm in thickness first at the frame 4 made from SUS316, and the product made from SUS316. The support plate 2 which consists of a metal porous body (nonwoven fabric which are 1.5 micrometers of diameters of average fiber and 30 micrometers of average apertures) which is about 30 micrometers was joined by welding. Between the frames 4 which joined this support plate 2, as shown in drawing 4, on both sides of the hydrogen permeable film 1 which consists of Pd-20wt%Ag alloy \*\*\*\*\* with a thickness of 40 micrometers in which the grid crevice with a depth of 25 micrometers was made to form in the pitch of 25 micrometers, it joined with the one-side square of 15 micrometers, and the hydrogen demarcation membrane unit of abbreviation 120mmx70mm magnitude was produced. The level difference which is equivalent to a of drawing 6 in this example was 20 micrometers.

[0015] The hydrogen permeable film in which the crevice was made to form was produced as follows. Namely, Pd-20wt%Ag alloy \*\*\*\*\* with a thickness of 40 micrometers is cleaned ultrasonically in alkali-cleaning liquid. The resist material (Tokyo adaptation make TSMR8800) of POJITAIPI is made into both sides with  $P$  by the coating machine after desiccation in a vacuum. After exposing ultraviolet rays on one side after stoving using a with a square [ of one-side pitch 25micrometer and 15 micrometers ] mask for 30 minutes at 90 degrees C, the resist material of the 15-micrometer one-side square section was removed in resist exfoliation liquid (Tokyo adaptation make NMD-W). Then, it held for 30 minutes in 120-degree C fluoric acid, and etching clearance of the 15-micrometer one-side square section was carried out. Consequently, the depth of a square crevice was about 25 micrometers.

[0016] The hydrogen permeable film 1 was made into Pd-20wt%Ag alloy \*\*\*\*\* with a thickness of 20 micrometers as a comparison sample, and also the hydrogen demarcation membrane unit of the structure of drawing 8 was produced like the above.

[0017] Thus, the performance evaluation was performed by the rupture test and hydrogen permeability ability of a foil about the produced sample. first -- fracture of a foil -- the inside of Ar -- differential pressure  $P=P_1-P_2=9$  kgf/cm<sup>2</sup> by the side of a raw material and purification hydrogen ( $P_1$ ) ( $P_2$ ) \*\*\*\*\* ( $P_2$  is a vacuum) -- it heated at 600 degrees C by the programming rate of 300 degrees C / Hr, and the hysteresis lowered to a room temperature by the cooling rate of 300 degrees C / Hr was repeated after maintenance for 30 minutes. Moreover, hydrogen permeability ability is differential pressure 9 kgf/cm<sup>2</sup> It carried out, the material gas side was used as the standard hydrogen gas containing 99% or more of hydrogen, and the hydrogen permeation rate was measured from the amount of the hydrogen penetrated to a purification hydrogen side at 550 degrees C.

[0018] The configuration and performance-evaluation test result of a sample which were used for the trial are shown in a table 1. As shown in a table 1, in a rupture test, a foil fractures to the 9th time by the sample of the example of a comparison by the conventional approach, and it is  $P_2$ . The pressure rose. On the other hand, by the sample of the example by this invention, it did not fracture by 50 repetitions, either. Moreover, in the example of this invention, 230cm<sup>3</sup>/(cm<sup>2</sup> and min-atm0.5) and a high value were acquired to a hydrogen permeation rate being 180cm<sup>3</sup>/(cm<sup>2</sup> and min-atm0.5) in the example of a comparison.

[0019]

[A table 1]

	支持板 (金属多孔体)		水素透過膜 (Pd-Ag膜)					試 験 結 果	
	厚さ ( $\mu\text{m}$ )	枠との 段差 ( $\mu\text{m}$ )	厚さ ( $\mu\text{m}$ ) $t_3$	升目状凹部 ( $\mu\text{m}$ )				温度昇降繰返し 箱の破断までの 回数	水素透過性能 $\text{cm}^3/(\text{cm}^2 \cdot \text{min} \cdot \text{atm}^{0.5})$
				凹部 深さ $t_1$	凹部 厚さ $t_2$	凹凸の ピッチ $l_1$	凹部の 一辺		
比較例	800	20	20	-	-	-	-	7	180
実施例			40	25	15	25	15	50回でも 破断せず	230

[0020]

[Effect of the Invention] as compared with the conventional hydrogen demarcation membrane unit, reinforcement is improved remarkably, the resistance over the repetition activity of long duration boils the hydrogen demarcation membrane unit of this invention markedly, and is excellent, and, moreover, hydrogen permeability ability is more than an EQC.

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**CLAIMS**

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[Claim(s)]

[Claim 1] The hydrogen demarcation membrane unit which is fixed across the perimeter of the hydrogen permeable film made from a metal or an alloy foil by the metal frame from both sides, and is characterized by to use the hydrogen permeable film of the metal which established many crevices in the transparency part of hydrogen as said hydrogen permeable film, or the product made from an alloy foil in the hydrogen demarcation membrane unit supported with the support plate which consists of metal porosity material of said hydrogen permeable film by which the perimeter was joined to said metal frame in the field by the side of purification hydrogen at least.

[Claim 2] The hydrogen demarcation membrane unit according to claim 1 characterized by forming the crevice established in the hydrogen permeable film the shape of a dimple, and in the shape of a grid.

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[Translation done.]